

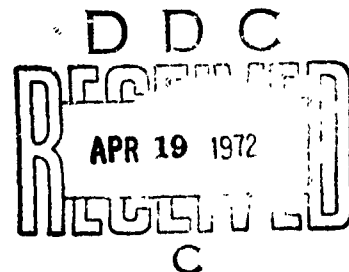
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VIBRATIONAL SPECTRA OF SUBSTITUTED CYCLOBUTANE COMPOUNDS

J. E. KATON AND ROSCOE O. CARTER

MIAMI UNIVERSITY



TECHNICAL REPORT AFML-TR-71-279

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FOREWORD

This report was prepared by the Department of Chemistry, Miami University, Oxford, Ohio under USAF Contract F33615-70-C-1021. This contract was initiated under Project No. 7360, "Chemical, Physical and Thermodynamic Properties of Aircraft, Missile and Spacecraft Materials," Task No. 736005, "Compositional, Atomic and Molecular Analysis of Experimental Materials for Advanced Air Force Systems." The work was administered under the direction of the Air Force Systems Command, Air Force Materials Laboratory, Materials Physics Division, Analytical Branch (AF'L/LPA), Wright-Patterson AFB, Ohio, Mr. Freeman F. Bentley, Project Engineer.

This report summarizes a portion of the work on the project carried out from 1 September 1969 to 1 March 1971 under the above contract.

It was submitted by the authors in November 1971.

The work was performed at Miami University. The major participants were Mr. Roscoe O. Carter and Dr. J. E. Katon. Dr. J. E. Katon served as project leader.

This technical report has been reviewed and is approved.



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ABSTRACT

As a preliminary to the study of group frequencies present in substituted cyclobutanes, the complete vibrational spectra of the model compound cyclobutanecarboxylic acid have been recorded on the crystalline material. A tentative, approximate vibrational assignment has been proposed based on these spectra along with the infrared spectra of the potassium salt, cyclobutanecarboxylic acid-0-d, cyclobutanecarboxylic acid- α -d-0-d, cyclobutanecarboxylic acid- α -d and previous published results with other simple cyclobutane derivatives.

The spectra of crystalline cyclobutanecarboxylic acid can best be interpreted in terms of a hydrogen bonded dimer structure with a center of symmetry. The results of the isotopic studies indicate that there is an unusual amount of vibrational coupling between vibrations of the hydrogen bonded ring system and a number of vibrations of the cyclobutane ring system.

The infrared spectra of fourteen substituted cyclobutanes have been recorded over the range $4000-200\text{ cm}^{-1}$ at both room temperature and about 110° K . Attempts have been made to find useful spectra-structure correlations which would serve for identification of the cyclobutane ring system. Six rather narrow regions of absorption have been identified in which nearly all of the compounds absorb, but the correlation bands vary in intensity rather widely. The consistencies of the absorptions nevertheless indicate some potential for their use in detecting, or confirming, the presence of the cyclobutane ring system.

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SECTION I

INTRODUCTION

Although there have been several reports of the infrared spectral properties of substituted cyclobutane compounds in an effort to deduce absorption frequencies characteristic of the cyclobutane ring, only a few simple substituted cyclobutanes have undergone a complete vibrational analysis. Because of our general interest in the vibrational spectra and structures of organic acids and salts, we became interested in performing a spectral analysis of cyclobutane-carboxylic acid.

Thomas, Williams and Orville-Thomas¹ have published a partial analysis of the infrared spectrum of cyclobutane-carboxylic acid as a part of a larger study of cyclobutane-carboxylic acids in general. Their interpretation was limited due to a lack of Raman data and a lack of low temperature facilities for the recording of the infrared spectrum of the solid. They were able to draw conclusions concerning the dimer-monomer equilibrium of the acid in the vapor and dilute solution states; to show evidence for a rotational conformational equilibrium in dilute solution; and to observe results, based on an unpublished assignment², which indicated that the molecular structure in the liquid state was such that the alpha hydrogen atom was internally hydrogen-bonded to one of the oxygen atoms.

This last conclusion requires a structure similar to I or III in Figure 1, where the structures are shown in projection, assuming a dimer with a center of symmetry. Of these structures, only I is analogous to those generally proposed for aliphatic carbonyl compounds and it corresponds to a less stable conformer. Since the bond angles involved are different for a four-membered ring than for an acyclic system, the same conformational stabilities are not necessarily expected.

The evidence for the C-H...O hydrogen bond was based on the assignment of the alpha carbon-hydrogen stretch at 2873 cm^{-1} in the liquid². This band apparently shifted to 2909 cm^{-1} in the vapor state and this large shift to higher frequency is typical of the results which occur with bond stretching vibrations when a hydrogen-bond is ruptured.

In this paper we report the complete infrared and Raman spectra of solid cyclobutanecarboxylic acid and propose a tentative assignment of the observed spectral features. The assignment is derived by comparison of the observed spectra with the solid phase infrared spectra of potassium cyclobutanecarboxylate and the following deuterated derivatives of cyclobutanecarboxylic acid: $\alpha\text{-D}$, O-D ; $\alpha\text{-D}$, O-H ; and $\alpha\text{-H}$, O-D , where α refers to the substituent on the alpha carbon atom. The assignment is limited to the solid since the spectrum of the liquid acids are so diffuse, due to hydrogen bonding, that a valid assignment would be very difficult. The solid state spectra are much sharper and better defined.

SECTION II

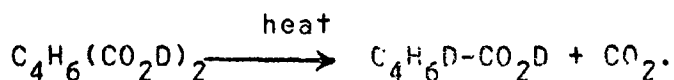
EXPERIMENTAL

Materials. All cyclobutane derivatives used as starting materials were purchased from the Aldrich Chemical Company, Inc. Cyclobutanecarboxylic acid was distilled under reduced pressure prior to use and constant boiling fractions (56°C at 5mm Hg) were utilized.

Both sodium and potassium cyclobutanecarboxylate were prepared by reacting stoichiometric quantities of sodium and potassium carbonate with cyclobutanecarboxylic acid in anhydrous methanol. The methanol was then evaporated and the salts dried at 100°C in vacuum. Both salts are hygroscopic and difficult to handle, but the potassium salt proved less so and was therefore used for spectral investigations.

Cyclobutanecarboxylic acid-0-d was prepared by the deuterolysis of cyclobutanecarboxylic acid anhydride. A semimicro distillation apparatus was dried in an oven at 130°C for two hours and then rinsed with deuterium oxide in a dry nitrogen atmosphere. The cyclobutanecarboxylic acid anhydride was placed in the flask along with D₂O (10% excess) and a small amount of sodium carbonate. The mixture was heated at 40°C for 30 minutes in a dry atmosphere, and then distilled to obtain cyclobutanecarboxylic acid-0-d.

Cyclobutanecarboxylic acid-α-d-0-d was prepared by a modification of the method of Farkis.³ Five grams of 1,1-cyclobutanedicarboxylic acid were dissolved in 15 ml. of D₂O, allowed to stand for 72 hours at room temperature, and then freeze dried. This process was repeated twice. The 1,1-cyclobutanedicarboxylic acid(-0-d)₂ was then transferred to a distillation apparatus which had been dried and rinsed with D₂O as described above. The material was slowly heated to 210°C whereupon the liquid began to bubble vigorously and to gently reflux. The reaction may be represented as



When the reaction had subsided the flask was cooled and the cyclobutanecarboxylic acid- α -d-0-d was distilled.

Cyclobutanecarboxylic acid- α -d-0-h was prepared by exchange using cyclobutanecarboxylic acid- α -d-0- and water (10 fold excess), followed by freeze drying. The procedure was repeated twice to obtain the desired acid.

Spectra. Infrared spectra ($4000\text{-}200\text{cm}^{-1}$) were recorded on a Perkin-Elmer Model 225 Infrared Spectrophotometer using a RIIC VLT-2 variable temperature infrared cell cooled with liquid nitrogen. Infrared spectra ($300\text{-}50\text{ cm}^{-1}$) were recorded on a Perkin-Elmer Model 301 Infrared Spectrophotometer using a similar cell. Raman spectra were recorded on a Cary Model 81 Laser Raman Spectrometer using an argon ion laser. The low temperature cell for the Raman spectrometer has been previously described⁴.

A typical infrared spectrum of solid cyclobutanecarboxylic acid in the $4000\text{-}200\text{ cm}^{-1}$ region is reproduced in Figure 2 and the corresponding infrared spectrum of the liquid is given for comparison in Figure 3. The Raman spectrum of solid cyclobutanecarboxylic acid is reproduced in Figure 4. Typical infrared spectra of the solid isotopically substituted acids are given in Figures 5-7.

The proposed assignment for the fundamental vibrations of cyclobutanecarboxylic acid is given in Table I and the pertinent data for the other compounds are given in other tables in the text.

The error in the reported frequencies is estimated to be no more than $\pm 2\text{ cm}^{-1}$ in the infrared and $\pm 5\text{ cm}^{-1}$ in the Raman. If the observed frequencies differ by more than $\pm 5\text{ cm}^{-1}$ they are assumed to be non-coincident and due to different vibrations.

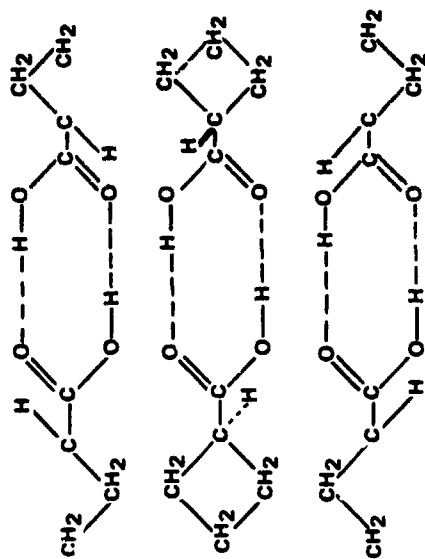


Figure 1. Possible Conformations of Cyclobutanecarboxylic Acid Dimers

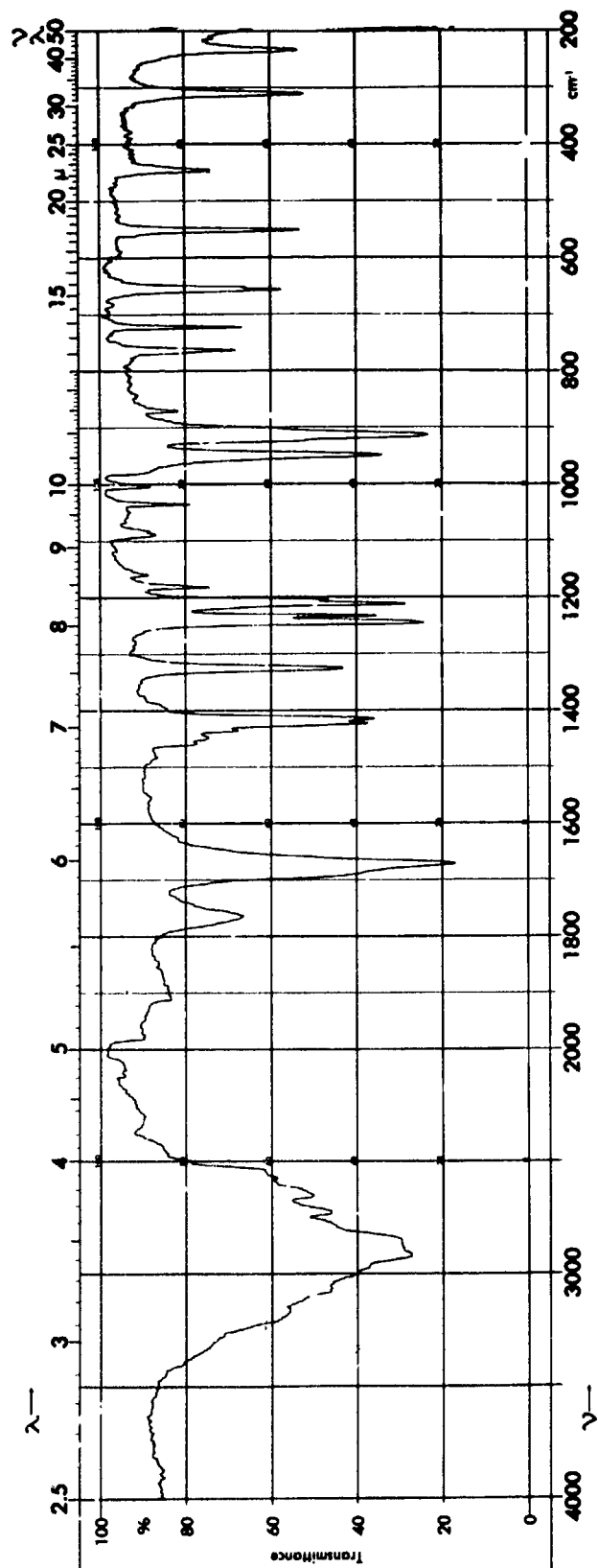


Figure 2. The Partial Infrared Spectrum of Crystalline Cyclobutanecarboxylic Acid.

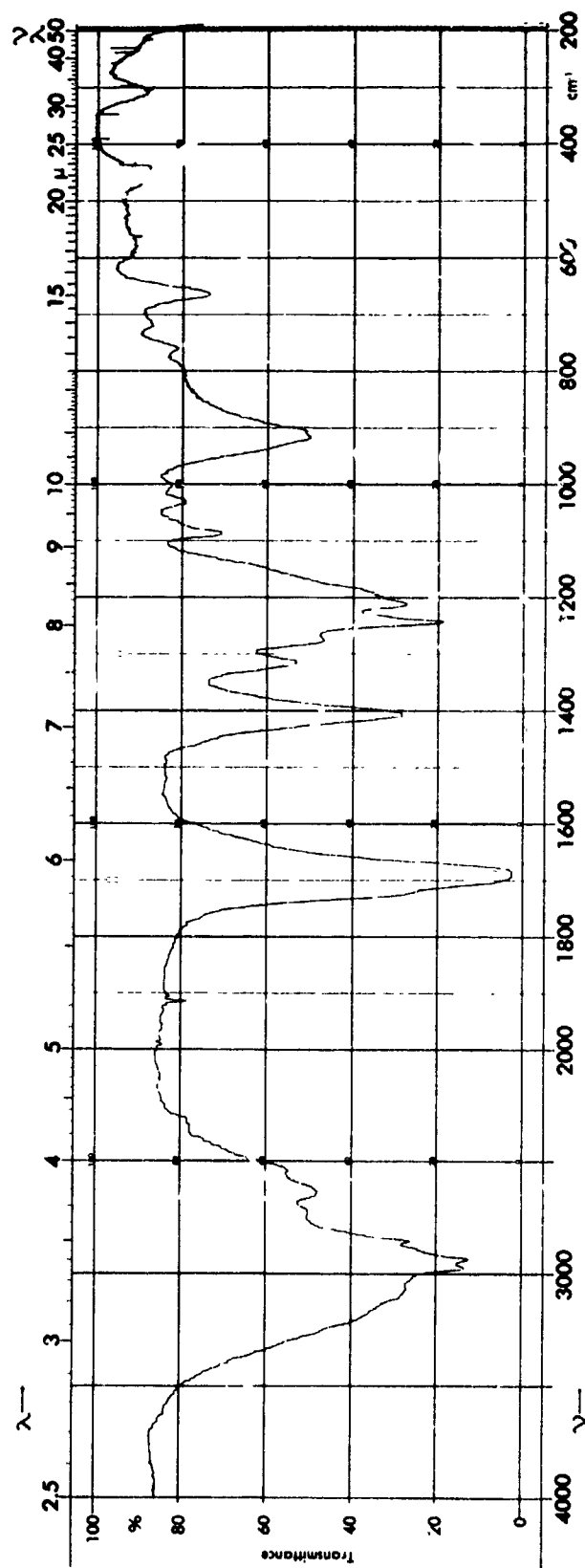


Figure 3. The Partial Infrared Spectrum of Liquid Cyclobutanecarboxylic Acid.

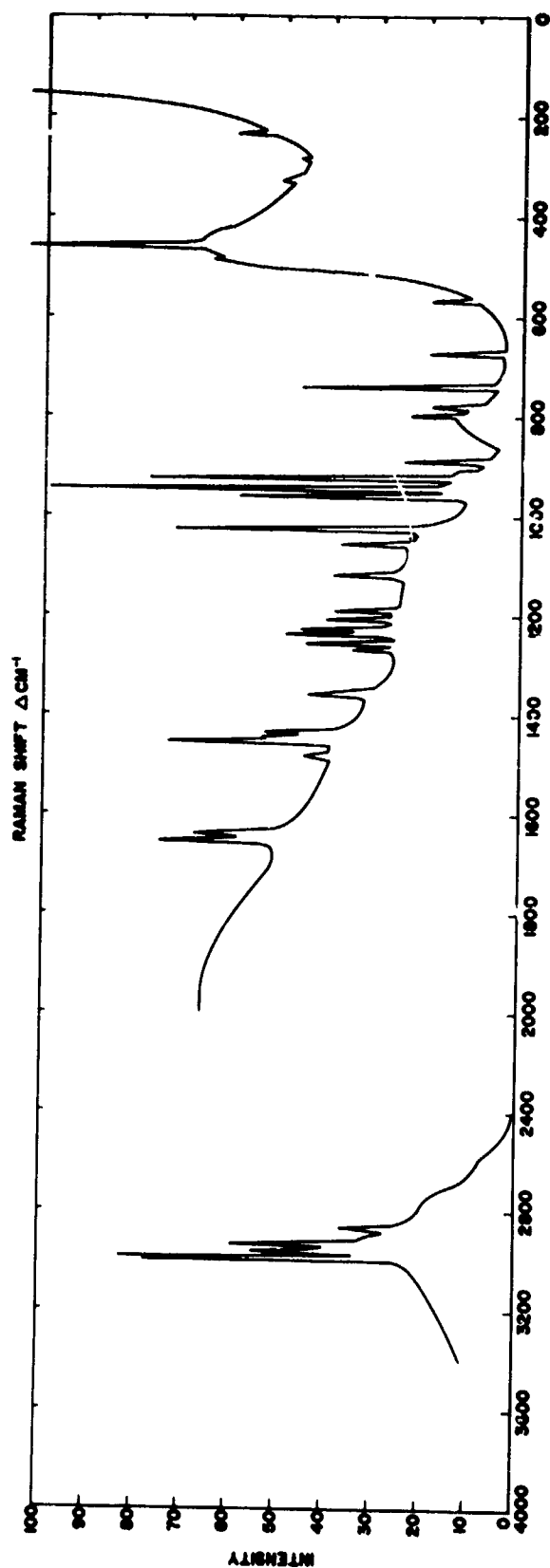


Figure 4. The Raman Spectrum of Crystalline Cyclobutanecarboxylic Acid (The broad features just above 400 and 800 cm^{-1} are due to the glass capillary which contained the sample).

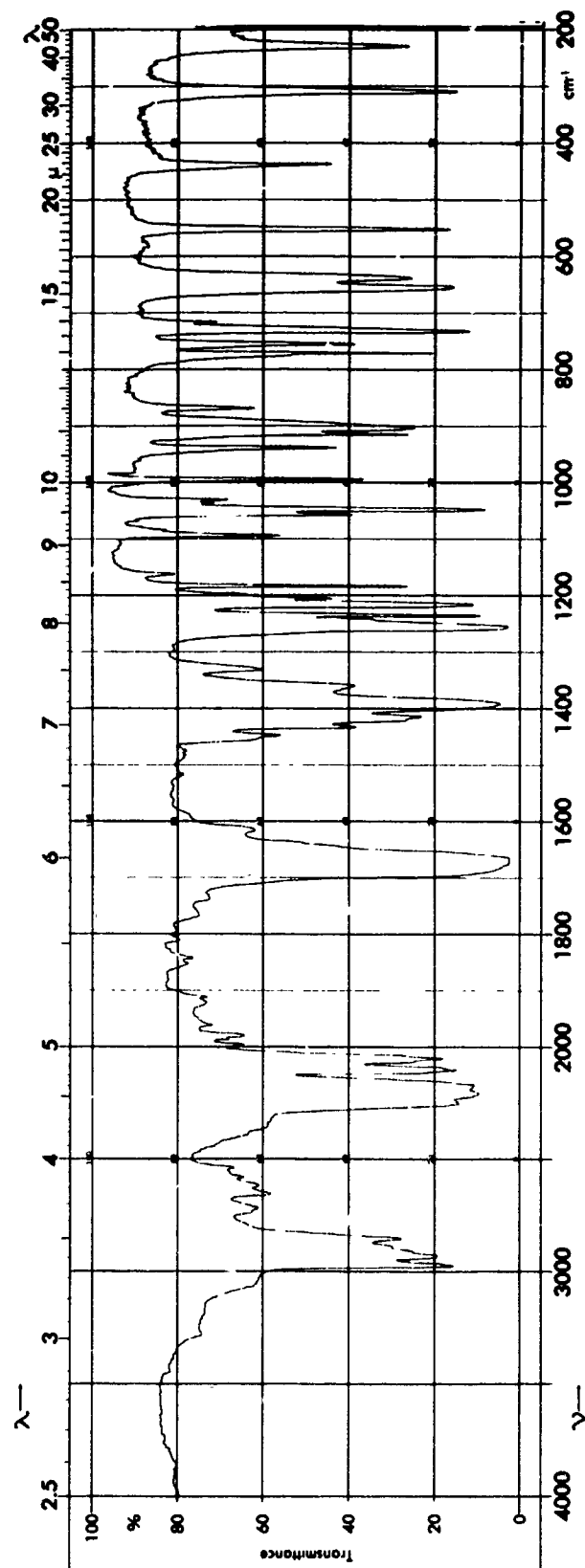


Figure 5. The Partial Infrared Spectrum of Crystalline Cyclobutane-carboxylic Acid-O-d.

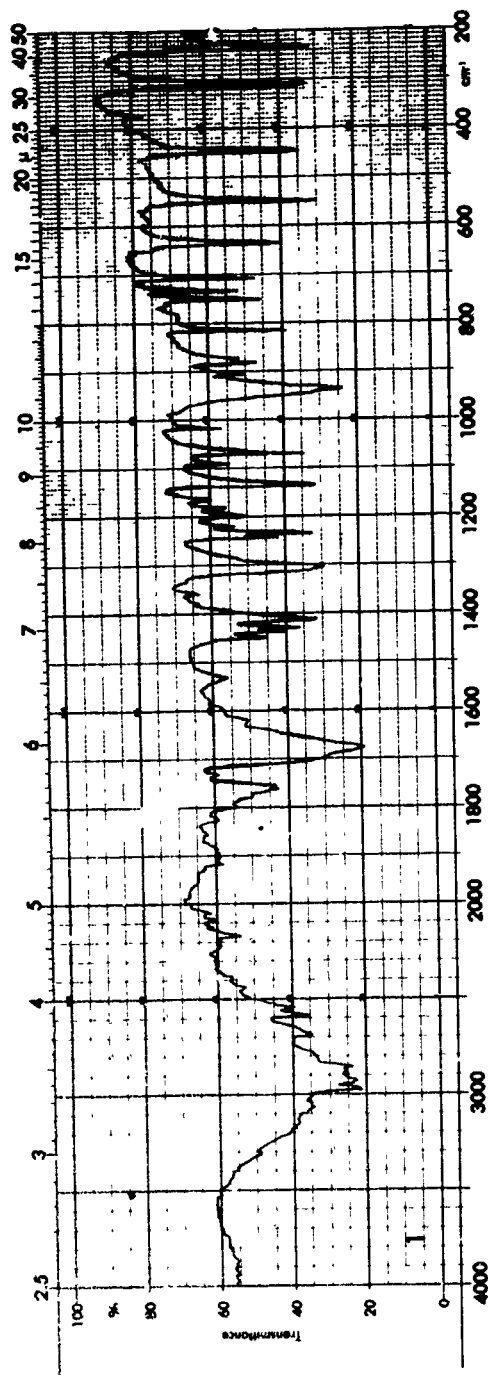


Figure 6. The Partial Infrared Spectrum of Crystalline Cyclobutane-carboxylic Acid- α -d.

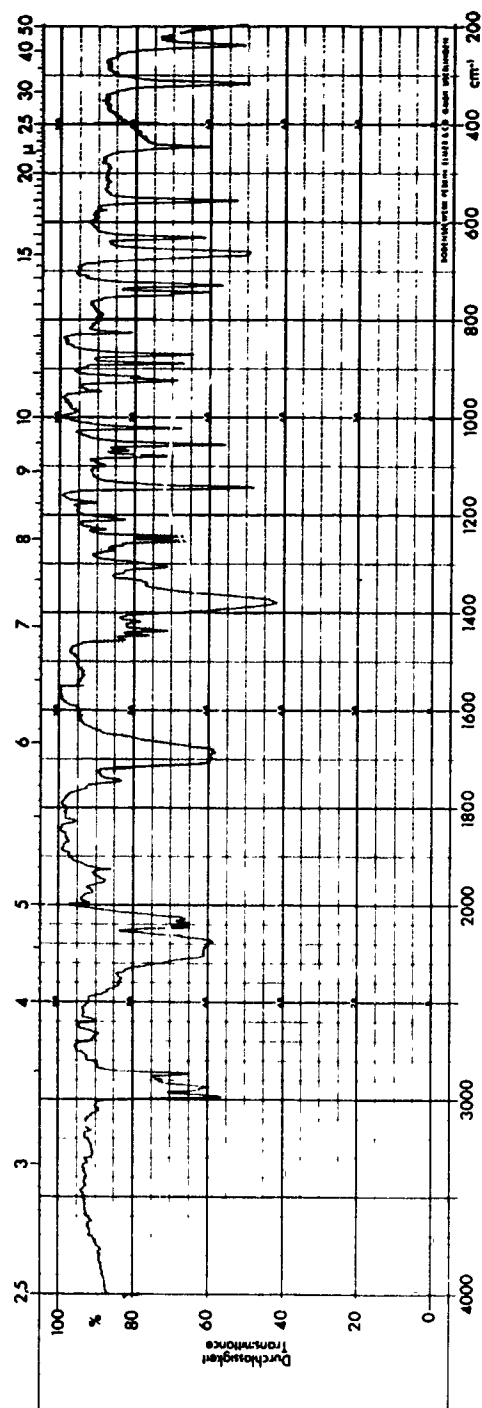


Figure 7. The Partial Infrared Spectrum of Crystalline Cyclobutane-carboxylic Acid- α -d-0-d.

Table I

Proposed Assignment of the Vibrational Fundamentals of Cyclobutanecarboxylic Acid. (The number in the assignment column corresponds to the number of fundamental vibrations of the dimer which have the corresponding description).

IR	R	Assignment
3300-2800s	3200-2700w	VOH, (2)
2991s*	2955vs 2991sh 2982vs }	νCH_2 , γ (4)
2980sh*		
2970w*		
2956s*	2960s 2933m-s 2866m }	νCH_2 , β (8)
2925*		
2905*		
2872m*		
1689vs	1654m }	$\nu\text{C=O}$ (2)
1475w	1481w }	δCH_2 scissors, γ (2)
1465w	1452s }	δCH_2 scissors, β (4)
1451w		
1441w		
1428m*		
1430s	1357m }	$\delta\text{OH in-plane}$ (2)
1342m		$\nu\text{C-O}$ (2)
1261s	1268w }	δCH (2)
1250m	1254m	βCH_2 wag (2)
1228s	1237m }	γCH_2 wag (2)

Table 1 (con't.)

IR	R	Assignment
1222w 1202w-m	1227m 1207w-m }	βCH_2 wag (2)
1178w	1189w-m }	γCH_2 twist (2)
1107w	1118w-m }	ν ring (2)
1052m 1021w	1056w 1026s }	RCH_2 twist (4)
967m	959s }	ring breath (2)
940w	944vs	ring-carbon stretch (2), ring deformation (2)
930s	-	δOH , in-plane (2)
930m* 920sh*	- }	RCH_2 rock (2)
920w	922s	δCH (2)
888w	889w-m	ring deformation (2)
780w-m	798w 779w }	βCH_2 rock (2)
740w-m	740m-s	ring deformation (2)
672m 667sh	672m }	γCH_2 rock (2)
568m	568m	δCO_2 scissors (2)
464w-m	460s	δCO_2 rock (2)
327m	326vw	δCO_2 wag (2)

Table I (con't.)

IR	R	Assignment
248m	236w }	ring-carbon bend (4)
155m	-	ring pucker (2)
111w,b	-	vH-bond (2)
-	-	H-bond bends (4)
-	-	torsions (2)

*Taken from the spectrum of an isotopically substituted compound.

SECTION IV

VIBRATIONAL ASSIGNMENT

Although it is not necessarily true that a given carboxylic acid exists as a hydrogen-bonded dimer in the liquid or the most stable crystalline phase, it has been shown that one can determine this structural feature by comparison of the infrared and Raman spectra in any given phase. In simple acids the dimer possesses a center of symmetry and the Rule of Mutual Exclusion holds so that the infrared and Raman spectra show a number of non-coincidences. This was first noted with regard to the carbonyl stretching vibration by Davies and Sutherland⁵ and has been discussed in some detail by Fairheller and Katon⁶. Although such behavior in the solid might be ascribed to crystal splitting effects, the fact that it occurs in the liquid phase and is only slightly shifted upon crystallization indicates that the results are due to an intramolecular, not an intermolecular, phenomenon.

As a result, the observed spectra must be treated as arising from a dimer molecule, even to a zero-order approximation. With cyclobutanecarboxylic acid this leads to the conclusion that one must interpret the spectrum in terms of a 30 atom molecule, leading to 84 fundamental vibrations. If the selection rules were to hold rigorously, there should be 42 infrared active fundamentals and 42 Raman active fundamentals. Seventy-eight of the fundamentals vibrations may be very approximately described as occurring in pairs, in which each pair consists of the same motion of the monomer groups, but differing with respect to phase (the remaining six are the so-called hydrogen-bond frequencies corresponding to the motion of one monomer unit against the other⁷). Thus, a particular pair of dimer fundamental vibrations will consist of an in-phase motion of the two constituent

monomer units, symmetric to the center of symmetry and Raman active, plus an out-of-phase motion of the two constituent monomer units, antisymmetric to the center of symmetry and infrared active. Since the selection rules will not hold rigorously in condensed phases, however, one would expect to observe some, if not all, of the fundamental vibrations in both spectra. Furthermore, because the components of a given pair couple with other vibrations in different ways, the two components will not occur at the same frequency. Clearly, such complicated spectra would be extremely difficult to assign rigorously. The situation is further complicated in the crystalline solid by potential crystal splitting effects arising from the possibility of interactions between two or more molecules in the unit cell.

A comparison of Figures 2 and 3 shows that the infrared spectrum of cyclobutanecarboxylic acid undergoes unusually large changes on crystallization. There are no large shifts and no readily apparent band disappearances (as one would expect if the liquid existed as an equilibrium mixture of two or more conformers), but there is extensive band sharpening and splitting. The large number of observed bands in the infrared and Raman spectra of crystalline cyclobutanecarboxylic acid makes it possible to carry out an assignment consistent with a very large number of fundamental vibrations, but in many cases one cannot differentiate with certainty between differing intramolecular fundamental vibrations and the same intramolecular fundamental split by crystal forces. The detailed assignment which is given here neglects crystal splitting, but it must be remembered that the small splittings observed may be due to intermolecular crystal effects rather than to slightly different intramolecular absorption frequencies. Nevertheless, the major features of the assignment, which are listed in Table I, and thus the gross structure of the molecule seem clear, particularly when the isotopic data

is considered, and so the remaining uncertainty involves only the details of the assignment.

Vibrational assignments have been published for four simple cyclobutane derivatives. Although there is some disagreement between authors, the most consistent series seems to be that of Durig and co-workers on cyclobutyl chloride⁸, bromide⁹, fluoride¹⁰, and cyclobutanol¹¹. The most significant of these is probably that of cyclobutanol since a larger number of isotopically substituted derivatives of this molecule were also studied. We have, therefore, made the assignment of cyclobutanecarboxylic acid consistent with the assignment of the alcohol in those cases where there seems to be no other criterion for choice between two or more alternative assignments.

For convenience, the following abbreviations are used in the subsequent discussion: CBCA - cyclobutanecarboxylic acid; Salt - potassium cyclobutanecarboxylate; α h0d - cyclobutanecarboxylic acid-0-d; α d0d - cyclobutanecarboxylic acid- α -d-0-d; α d0h - cyclobutanecarboxylic acid- α -d-0-h; dip - dimer in-phase vibration; dop - dimer out-of-phase vibration; rip - ring in-phase vibration; rop - ring out-of-phase vibration. The latter two designations are used for vibrations which are best described in terms of the local vertical plane of symmetry of the cyclobutane ring, e.g. the beta CH_2 vibrational modes. α , β and γ refer to the positions on the cyclobutane ring, ν and δ refer to bond stretching and bond bending vibrations.

3300-2700 cm^{-1} Region. The observed data in this region are given in Table II, where the assignment column refers to the assignment of CBCA.

The νOH absorption obscures all of the νCH bands in the infrared spectrum, but because of its typically much weaker Raman scattering, the νCH bands can be easily discerned in the Raman spectrum. Both νOH and νOD have the

Table II

CBCA		αhOd		αdOd		αdOh		Salt		Assignment
IR	R	IR		IR		IR		IR		
3300-2800s		2300-2050s		2450-2050s		3300-2800s				νOH, dop
3200-2700w										νOH, dip
2995vs										νCH ₂ , γ antisym, dip
2991sh		2991s		2988s				2992m		νCH ₂ , γ antisym, dop
2982vs		2980sh		2978sh				2980m		νCH ₂ , γ sym, dip, dop
2970sh		2970w								νCH, dip, dop
2960s		2956s		2956s		2185w				νCH ₂ , β antisym, rip dip, rip dop
2933m-s										νCH ₂ , β antisym, rop dip
		2925m		2938s				2938m		νCH ₂ , β antisym, rip dip
										rip, dop
		2905w		2899w				2905w, sh		νCH ₂ , β antisym, rop dop
		2872m		2865m				2890vw		νCH ₂ , β sym, rop dip
										rop dop
2866m								2862w		νCH ₂ , β sym, rip dop

typical structure associated with these vibrations in organic acids and no attempt was made to assign these structural features.

Probably the most significant feature is the assignment of the αCH stretching mode. Our assignment clearly disagrees with that of Stein², but is equally clearly assigned correctly in view of the isotopic shift. It is assigned in other cyclobutyl derivatives in the range $2943\text{--}3020\text{ cm}^{-1}$. The αCH is a weak band, but is quite reproducible in the spectrum of $\alpha\text{H}_0\text{d}$ and definitely disappears in the spectrum of $\alpha\text{D}_0\text{d}$. These results lead to the conclusion that there is no evidence for an intramolecular hydrogen-bond involving the alpha hydrogen of CBCA.

The β and γCH_2 stretches are assigned to be consistent with the corresponding absorption bands in cyclobutanol with γ , β antisymmetric, and β symmetric stretches occurring with descending frequencies. The qualitatively more symmetric of these vibrations are assigned to the stronger Raman bands, the qualitatively more antisymmetric are assigned to the strong infrared bands. Not all of the in-phase, out-of-phase pairs are split, but this is typical of the spectra of acid dimers⁶.
 $1700\text{--}1300\text{ cm}^{-1}$ Region. The observed data in this region are given in Table III. The carbonyl stretching vibrations differ in the infrared and Raman spectra in the manner expected for a dimer structure⁵. The various CH_2 scissors modes are assigned as in other cyclobutane compounds with the modes due to the γ hydrogens being higher in frequency than those due to the β hydrogens.

The OH in-plane bending mode is readily determined by comparison with the OD compounds since it shifts to lower frequencies. As is usual with acid dimers, the $\nu\text{C=O}$ vibration is strongly coupled with δOH but not with δOD . As a result, it shifts upward in the OD compounds. The behavior of both δOH

Table II'

CBCA		adOd		adOr		Salt		Assignment
IR	R	IR	IR	IR	IR	IR	IR	
1689vs		1690vs	1680vs	1685vs	1540vs,b			νC=O, dop
	1654m							νC=O, dip
	1481w				1475vw			γCH ₂ scissors, dip
1475w				1468w				γCH ₂ scissors, dop
1465w		1452m		1448w-m	1440w			ACH ₂ scissors, rip dop
1451w	1452s		1455w	1439m	1426w			ACH ₂ scissors, rip dip
1441w		1436m	1448w	1421m-s				ACH ₂ scissors, rop dip
1430s		1061s	1056s					δOH, in-plane, dop,
		1009m						dip
		1428m	1438m					ACH ₂ scissors, rop dop
	1357m							νC-O, dip
1342m		1408s	1380s	1312s	1370m			νC-O, top

and $\nu\text{C-O}$ on deuteration is well-known and has been thoroughly discussed by Hadzi and Sheppard¹².

One of the βCH_2 scissors modes is obscured by δOH in the light compound, but becomes apparent in the deuterated derivatives and may be then readily assigned.

The δOH absorption does not split into an in-phase and out-of-phase pair, but the δOD does in αhOd . This difference in splitting of pairs of dimer vibrations on isotopic substitution has been noted previously with iodoacetic acid¹³. Detailed studies of various deuterated acetic acid monomers has shown alpha hydrogen modes couple with δOH and $\nu\text{C-O}$ in different ways¹⁴. In view of this, and the fact that vibrational coupling must be the major cause of the frequency splitting of phase related pairs, it is not surprising that these results occur.

1300-1000 cm^{-1} Region. The observed data are given in Table IV. The $\alpha\text{C-D}$ bending modes split considerably further than do the $\alpha\text{C-H}$ bending modes, again presumably because of different coupling behavior. The various CH_2 wagging and twisting modes are assigned in the same frequency order as in the other cyclobutyl derivatives¹⁰ and the highest ring deformation in all these compounds has been assigned to a band near 1100 cm^{-1} .

1000-600 cm^{-1} Region. The observed data in this region are found in Table V. The ring modes agree well with other compounds of the cyclobutyl series. The δOH and δCH modes are readily assigned from the deuteration data, but again, the splitting of the phase related pairs is a strong function of the isotopic substitution in the case of the δCH modes.

The antisymmetric βCH_2 rocks deviate from the other cyclobutyl compounds rather widely (about 100 cm^{-1}). This is an extremely large deviation compared to the other cyclobutane ring modes and this assignment is therefore somewhat suspect. These absorption bands can only be observed in the Od compounds since they are hidden under δOH in the light compounds. It is

Table IV

CBCA		αH ₀ d		αD ₀ d		αD ₀ h		Salt		Assignment
IR	R	IR	IR	IR	IR	IR	IR	IR	IR	
1261s	1268w		1271s	1175w	1143m					δCH, dip
1250m	1254m	1250m-s		1080m	1080m			1288m		δCH, dop
	1237m			1243m	1244m					βCH ₂ wag, rip dip, rip dop
1228s		1231m-s		1230w	1230w			1229w		γCH ₂ wag, dip
1222w	1227m	1220w		1209w-m	1209w-m			1208w		γCH ₂ wag, dop
1202w-m	1207w-m	1200m		1194w	1194w					βCH ₂ wag, rop dip
	1189w-m									βCH ₂ wag, rop dop
1178w		1176w			1177w			1166m		γCH ₂ twist, dip
	1118w-m									γCH ₂ twist, dop
1107w		1110w		1099w	1100w			1098w		ring, dip
1052m	1056w	1050vw						1056w		ring, dop
1021w	1026s	1046w		1021m-s	1028w			1029m		βCH ₂ twist, rop dip, rop dop
										βCH ₂ twist, rip dip, rip dop

Table V

CBCA		α hOd		α dOd		α dOh		Salt		Assignment
IR	R	IR	IR	IR	IR	IR	IR	IR	IR	
967m		953m		988w				973w		ring breath, dop
	9F9s									ring breath, dip
940w	944vs			948w				942w		ring-carbon stretch, dop, dip
930s		770m-s		730m-s		948vs				δ OH, out-of-plane, dop, dip
		930m		935m				852		β CH ₂ rock, rop dop
		920sh		916w						β CH ₂ rock, rop dip
920w	922s	918m-s		890m-s		891w-m		903w		α CH bend, dop.
				828m		826m				dip
888w	389w-m	884w		871m-s		884w		888m		ring deformation, dip, dop
	796w	790sh								β CH ₂ rock, rip dip
780w-m	779w	786s		750w		762m		803m-s		β CH ₂ rock, rip dop
740w-m	740m-s	740s		742s		745m		765m-s		ring deformation, dip,
						719m				dop
672m	672m	670s		666s				671m		γ CH ₂ rock, dip
667sh		650m		662sh						γ CH ₂ rock, dop

felt that the present assignment gives the greatest internal consistency. These CH_2 rocking vibrations are known to couple strongly with other CH_2 modes in straight chain compounds and this may be the cause of the large shift.

There are not sufficient observed bands to completely assign all bands expected in this region. Two extra ring deformation bands are expected near 900 cm^{-1} and must be accidentally degenerate with other bands. They were selected to correspond with the strongest Raman band in this region since they should give strong Raman bands.

600-100 cm^{-1} Region. The data for this region are given in Table VI. The assignments in the $600\text{-}300\text{ cm}^{-1}$ region were made primarily by comparison with reported carboxylic acid spectra¹⁵. The band at 248 cm^{-1} is below the normal acid frequencies and so was assigned as a ring-carbon bending mode. All of these descriptions of skeletal bending modes must be considered as very approximate since they are surely highly mixed. The ring puckering vibration is close to that in other cyclobutyl derivatives. The hydrogen-bond stretching mode is low compared to straight chain acids, but it has been shown to be lowered by α -branching and falls in the expected region for such a compound (compare $(\text{CH}_3)_2\text{CH-CO}_2\text{H}$, which has ν_{H} band at 111 cm^{-1} , also)¹⁶.

No bands were observed which could be readily assigned to the remaining hydrogen bond bending modes or the torsional modes. All of these vibrational modes tend to be weak in the infrared spectrum as well as the Raman spectrum.

Table VI

CBCA		ahOd		adOd		adOh		Salt		Assignment
IR	R	IR	IR	IR	IR	IR	IR			
568m	568m	568s	559s	560m	510m-s	δCO_2 scissors, dip, dop				
464w-m	460s	451m-s	459m	446m	483m-s	δCO_2 rock, dip, dop				
327m	326vw	323s	318m	321m	333m	δCO_2 wag, dip, dop				
248m		243m-s	240m	242m	210m	ring-carbon bend, dop				
	236w					ring-carbon bend, dip				
155m						ring pucker, dop, dip				
111w, b						vH-bond				

SECTION V

CONCLUSIONS

The relatively large number of non-coincidences between the infrared and Raman spectra indicate that the molecule possesses a center of symmetry. This can best be explained by a hydrogen-bonded dimer in which the two rings are oriented in such a way as to maintain the center of symmetry of the hydrogen-bonded ring system. The exact conformation of the rings cannot be ascertained by this data, but it must be concluded that there is no evidence for an internal hydrogen bond involving the alpha hydrogen and therefore no evidence that structures I or III in Figure 1 represent a preferred conformation.

The gross assignment of frequencies is, in most cases, consistent with assignments of other cyclobutyl systems. The spectrum has been assigned, however, by neglecting both crystal effects and possible overtone and combination bands. It is therefore unlikely that the detailed assignment is correct in all of its aspects. A number of fundamental vibrations have been assigned as being accidentally degenerate. It is probable that some of the weaker bands observed are due to other than intramolecular fundamentals, leading to still further accidental degeneracies amongst the fundamentals. The choice between an intramolecular fundamental and another vibrational mode cannot be easily made with these absorption bands, however, and the present assignment does have a certain internal consistency.

The assignments of many of the fundamentals, especially those based on the deuteration studies seem well founded, however. It is interesting to note the dependencies of the frequency splittings of the phase-related pairs of vibrations on isotopic substitution. This provides further evidence of the complex vibrational couplings present in acid

dimers. Although this situation has been realized as existing by other authors, its full extent has probably not been widely recognized. It is probable that this is the reason for the rather extreme difficulties that have been encountered in making completely satisfactory vibrational assignments for even the simplest acids.

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INFRARED SPECTRA-STRUCTURE CORRELATIONS FOR SUBSTITUTED CYCLOBUTANE COMPOUNDS

SECTION I

INTRODUCTION

Because of widespread interest among organic chemists, the infrared spectra of saturated carbocyclic systems received a good deal of study several years ago. Although a certain amount of success was obtained in spectra-structure correlations for some of these classes, the data on the four-membered ring compounds was less clearly defined and their interpretation was ambiguous. This early work has been summarized by Bellamy¹. A more recent study by Ulery and McClenon² reports a computer summary of the spectra of substituted cyclobutanes drawn from widely diverse sources and of questionable quality.

Much of the confusion with regard to the interpretation of the spectra of this class of compounds arises from a lack of good vibrational assignment data on simple model compounds. Due to recent interest in detailed assignments of such compounds^{3,4} this problem has been greatly alleviated.

The availability of several derivatives of cyclobutane has prompted us to record their infrared spectra on the presently available high resolution instrumentation, both at ambient temperature and at relatively low temperature (about 120°K). We have then searched for useful spectra-structure correlations utilizing the assignment data for simple model compounds which are now available in the hope that more useful conclusions concerning possible correlations could be derived.

It has been noted by Rothschild⁵ that the spectra-structure correlations for cyclopropanes may be fortuitous in that correlation bands are not due to the same fundamental vibration. Nevertheless, as pointed out by Bellamy⁶, the usefulness of such correlations for identification is not obviated by this fact. More care is required in drawing

conclusions concerning structural features from the infrared spectra, however.

In view of the ambiguities previously reported with regard to the infrared spectra of cyclobutane compounds, it is expected that a similar situation occurs with these compounds.

II. EXPERIMENTAL METHOD

All compounds were obtained from commercial sources and were, for the most part, used without further purification. The spectra of the solids were recorded as Nujol and hexachlorobutadiene mulls at room temperature. The spectra of the liquids were recorded as capillary films and as solid films at low temperatures (about 120°K) by the use of an RIIC VLT-2 variable temperature ir cell utilizing liquid nitrogen as a coolant. From changes in the spectra on cooling, it appeared that all of the liquids crystallized at 120°K.

Infrared spectra were obtained on a Perkin-Elmer Model 225 ir spectrophotometer over the range 4000-200 cm^{-1} using cesium iodide cell windows. The spectrophotometer was calibrated with an indene-cyclohexanone-camphor mixture⁷ and the recorded frequencies should be correct to at least $\pm 3 \text{ cm}^{-1}$.

III. RESULTS AND DISCUSSION

One of the difficulties with characteristic absorption bands of cyclobutane derivatives is their variable and oft a rather weak intensities. This has been previously noted by Bellamy¹. The ranges for these absorptions are, however, reasonably narrow in many cases and therefore do provide potentially useful correlations. No attempt was made to deduce

correlations in the carbon-hydrogen stretching region since many of the compounds studied possessed OH absorption in this region which obscured the CH stretching frequencies and several others had substituents bearing CH groups which complicated the region too much for reliable interpretation.

Tables I and II give the measured frequencies for the liquid and solid compounds, respectively, in the regions of interest. This data is summarized in Table III in the form of a list of characteristic absorption ranges. The intensities of these absorptions are all quite variable within the series of compounds. Nevertheless, nearly all of the compounds absorb in all of the regions and the fact that there are six regions, most of which are reasonably narrow, seems to indicate that there is some potential for identification of the cyclobutane ring system.

Assignments are also given in Table II for those compounds which have undergone a detailed frequency assignment. In most cases the assignments are consistent, but this is not always the case. The correlation range 1 has been assigned to a βCH_2 twisting mode in all compounds except cyclobutyl fluoride. However, not all compounds which show this correlation have a βCH_2 group (e.g. α -truxillic acid). Ring deformations are consistently assigned in correlation ranges 2 and 4 and these would be expected to be rather reliable group frequency ranges, although range 4 is rather wide. Range 3 is consistently assigned as a βCH_2 rocking mode, but this leads to the same difficulties that have been mentioned in regard to range 1. The same situation occurs with range 5, which is consistently assigned as a γCH_2 rock. Range 6 has been assigned as a ring-carbon bending mode in cyclobutanecarboxylic acid, which explains its absence in cyclobutyl fluoride, bromide, chloride and cyclobutanol.

Table I

Observed Absorptions for Liquid Cyclobutane Derivatives
in the Characteristic Frequency Regions of Table III.

Compound	Range	Observed Absorptions
1. Cyclobutyl chloride ⁸	1	1100vbw
	2	938m
		902m
	3	815m
		780
	4	715s
	5	615vbw
	6	-
2. Cyclobutyl bromide ⁹	1	1086w
	2	937vw
	3	809vs
	4	698vs
	5	621w
	6	278w
		248w
3. Cyclobutanecarboxylic acid	1	1102m
	2	934m-s
	3	777w
	4	733w
	5	681m
	6	238w
4. 1,2-cyclobutane-dicarboxylic acid anhydride	1	1086s
	2	926w
	3	-
	4	-
	5	-
	6	-
5. Cyclobutanecarboxylic acid chloride	1	1101w
	2	960vs
	3	800s
	4	715s
	5	668w
	6	287vw

6.	1-hydroxymethyl- cyclobutanol	1	1119m
		2	922m
		3	784vw
		4	721m
		5	640vw
		6	-
7.	1-Phenylcyclobutane carbónitrile	1	1095vw
		2	920m
		3	785w-m
			750vs
		4	690vs
		5	653m
		6	290w
8.	Cyclobutyl-p-fluoro- phenyl ketone	1	1091m
		2	915w
		3	772w
		4	743m
			707w
		5	661m
			625w
		6	289w
9.	1,2-trans-cyclo- butanedicarboxylic acid chloride	1	1096w
		2	939s
		3	815m-s
		4	722s
		5	679sh
			648sh
		6	268w
10.	Cyclobutanol ¹⁰	1	1092vs
		2	958s
			928m
		3	775vw
		4	750m
		5	606w
		6	-

Table II

Observed Absorptions for Solid Cyclobutane Derivatives
in the Characteristic Frequency Regions of Table III.

Compound	Range	Observed Absorptions	Assignment
1. Cyclobutyl fluoride ³	1	1081sh	CF stretch
	2	943s	Ring breath
		933s	Ring def.
	3	782w	βCH_2 rock
	4	753}m 750}	Ring def.
	5	597m	γCH_2 rock
	6	-	
Cyclobutyl chloride ⁸	1	1100vvw	βCH_2 twist
	2	940w	Ring def.
		900w	Ring def.
	3	815w	βCH_2 rock
	4	715s	Ring def.
	5	-	
	6	-	
3. Cyclobutyl bromide ⁹	1	1087w	βCH_2 twist
	2	940w	Ring def.
	3	815vs	Ring breath
		808w	βCH_2 rock
	4	699s	Ring def.
	5	625vw	γCH_2 rock
	6	-	
4. Cyclobutanol ¹⁰	1	1085s	Ring def.
		1068w	βCH_2 twist
	2	932m	CH bend
		904vw	Ring def.
	3 (Raman only)	781	βCH_2 rock
	4	750m	Ring def.
	5	603w	γCH_2 rock
	5	-	

5.	Cyclobutanecarboxylic acid	1	1052m	RCH ₂ twist
		2	940w	Ring def.
			930m	BCH ₂ rock
			920w	CH bend
		3	780w-m	RCH ₂ rock
		4	740w-m	Ring def.
6.	Cyclobutanecarboxylic acid chloride	5	672m	γCH ₂ rock
		6	248m	ring-X bend
7.	1,1-cyclobutane-dicarboxylic acid	1	1099m	
		2	918vw	
		3	798s	
			774m	
		4	710s	
		5	659w	
8.	α-Truxillic acid		639m-s	
		6	282w	
9.	1,2-cyclobutane-dicarboxylic acid anhydride	1	1105w	
		2	916vs	
		3	800w	
			772w	
		4	734w-m	
		5	688m	
10.	1,3-cyclobutane-dicarboxylic acid	6	262w	
			243w	
11.	1,3-cyclobutane-dicarboxylic acid	1	1080m	
		2	930s	
		3	786w	
			769w-m	
		4	732 } m	
			725 }	
12.	1,3-cyclobutane-dicarboxylic acid	5	692s	
		6	230vw	
13.	1,3-cyclobutane-dicarboxylic acid	1	1093w	
		2	920s	
		3	800m	
		4	710m	
		5	700m	
		6	245w	

10. 1-Phenylcyclobutane-carboxylic acid	1	1050w-m
	2	929m
		910w
	3	780w
	4	730s
	5	695s
		622m
	6	270w
11. 1,2-cis-cyclobutane-dicarboxylic acid	1	1095m
		1086m
	2	910s
	3	772w-m
	4	725m
	5	647w
	6	280w-m
		262w-m
12. 1,2-trans-cyclobutane-dicarboxylic acid chloride	1	1098m
	2	937m-s
	3	812s
	4	718vs
	5	645w
	6	265w
13. Cyclobutyl-p-fluorophenyl ketone	1	1099m
	2	918w
	3	781s
	4	758s
		719m
	5	671m-s
		636w-m
	6	234w
14. 1,2-dicyanocyclobutane	1	1061m
	2	918m
	3	796m
	4	750w
	5	696vw
	6	280w-m

15.	1-Phenylcyclobutane- carbonitrile	1	1078m
		2	928m
		3	794m
		4	759vs
		5	660m
		6	-
16.	Cyclobutyl phenyl ketone	1	1100w-m
			1086w
		2	916m
		3	795w-m
			778m-s
		4	733s
17.	1,2-trans-cyclobutane- dicarboxylic acid	5	695s
			650m-s
		6	259m
		1	1099w
		2	931s
			918s
18.	1,1,3,3-cyclobutane- tetracarboxylic acid	3	775vw
		4	735m
		5	689m
			634w
		6	272w-m
			232w

The data for compounds 1-4 are from an argon matrix of the compound. Compounds 6, 7, 9, 10, 11, 14, 16 and 17 are liquid at room temperature and so the data given are from spectra recorded at 120°K.

Table III

Characteristic Absorption Ranges of Cyclobutane Derivatives

Absorption Range	Liquids	Solids
1	1120-1080	1105-1050
2	960-900	940-900
3	815-750	815-770
4	760-690	760-695
5	680-605	700-595
6	290-240	280-230

SECTION IV

CONCLUSIONS

There are six regions of the infrared spectrum in the $2000\text{--}200\text{ cm}^{-1}$ range in which nearly all of the substituted cyclobutanes studied absorb. Unfortunately, the intensities of the absorption bands are very variable and this certainly detracts from their utility as correlation bands. Nevertheless, five of the regions are quite narrow, and the fact that the absorptions are so consistent does lead to some potential for their use in at least confirmatory studies.

It is clear that the correlations in certain of the regions are fortuitous in the sense that the origin of the absorption cannot be the same in all of the compounds studied. This conclusion is based on the detailed assignments which have been carried out on several simple substituted cyclobutanes. The two ranges at $940\text{--}900\text{ cm}^{-1}$ and $760\text{--}695\text{ cm}^{-1}$ in the solids have been consistently assigned as ring deformation modes, however, and therefore are expected to be more reliable than those assigned to the various CH_2 deformation modes. It would probably be profitable to study the Raman spectra of these compounds as these ring deformation modes might be expected to give rather intense Raman bands and they might be even better correlation bands in the Raman spectra. The absorption range at $280\text{--}230\text{ cm}^{-1}$ appears to be due to the ring-substituent bending mode in which the substituent atom directly bonded to the ring is carbon. This might prove to be quite useful in differentiating cyclobutane derivatives with carbon atom substituents from those in which the attached atom is that of some other element.

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